



Catalytic oxidation and adsorption of Hg⁰ over low-temperature NH₃-SCR LaMnO₃ perovskite oxide from flue gas

Haomiao Xu, Zan Qu, Chenxi Zong, Fuquan Quan, Jian Mei, Naiqiang Yan*

School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

ARTICLE INFO

Article history:

Received 9 July 2015

Received in revised form

23 December 2015

Accepted 24 December 2015

Available online 29 December 2015

Keywords:

Perovskite

Elemental mercury (Hg⁰)

Manganese oxides

Catalytic oxidation

ABSTRACT

To simultaneously remove elemental mercury (Hg⁰) and NO_x at low temperature from flue gas in coal-fired power plants, an efficient NH₃-SCR LaMnO₃ perovskite oxide was chosen as the catalyst for Hg⁰ removal. The physicochemical properties, surface reaction and mercury desorption were investigated using BET, XRD, XPS, H₂-TPR and Hg-TPD, to investigate the Hg⁰ capture mechanism over LaMnO₃ oxides. The results indicated that LaMnO₃ exhibits a Hg⁰ capacity that is as high as 6.22 mg/g (600 min) at 150 °C. O₂ enhanced the Hg⁰ removal performance by re-oxidation of reduced Mn³⁺ to Mn⁴⁺ and providing additional adsorbed oxygen. NO enhanced the Hg⁰ removal performance. However, NH₃ exhibited negative effects on Hg⁰ removal. The NH₃ + O₂-TPD and NO + O₂-TPD results indicated that the ad-NH₃ species prevent Hg⁰ adsorption, but the ad-NO₂ species were beneficial for Hg⁰ oxidation. The effects of SO₂ and H₂O were also investigated, and the results indicated that they inhibited Hg⁰ removal. Hg-TPD under different reaction atmospheres was employed to further investigate the combining state of Hg⁰ on LaMnO₃ surface, the results indicated that mercury primarily existed as Hg-O, and LaMnO₃ can be regenerated using thermal desorption.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Elemental mercury (Hg⁰) in the atmosphere is hazardous for human and the environment [1–3]. The Minamata Convention on Mercury signed aiming at controlling mercury emission globally. Among the various emission sources, coal-fired power plants are major anthropogenic mercury emission sources [4,5]. In China, approximately 38% of the Hg⁰ is emitted from coal-fired flue gas [5]. Currently, Hg⁰ removal technologies are often part of the available equipment for co-beneficial mercury control (e.g., using SCR catalysts for the oxidation of Hg⁰ to oxidized mercury (Hg²⁺), followed by Hg²⁺ removal in wet flue gas desulfurization (WFGD) system) [6–8]. Another method was adsorption technology, and activated carbon injection (ACI) technology makes full use of AC to adsorb Hg⁰. In addition, the particle-bound mercury (Hg^P) is removed along with fly ash in the ESP/FF system [9,10]. However, the Hg²⁺ enriched in the WFGD system or mercury in the fly ashes could cause secondary mercury contamination [7,11]. Furthermore, the use of the ACI technology was limited due to its high cost, depen-

dences on the type of coal, inlet mercury concentration and reaction temperature [12,13].

In addition, more strict regulation aims to approach zero emission in coal-fired power plants, and the emission concentration should be NO_x ≤ 5 mg/m³ and Hg⁰ ≤ 0.002 mg/m³. However, in many coal-fired power plants, the space required for the installation of deNO_x unit that operate at flue gas temperature of 350–400 °C is insufficient. To avoid deactivation of SCR catalyst and reduce costs, the proposed additional deNO_x technologies could be loaded downstream of the particle control devices where the flue gas temperature is lower than 200 °C. However, traditional SCR catalysts (V-W-TiO₂/V-Mo-TiO₂) may lose their activity at this low temperature. Moreover, without SCR catalysts in the coal-fired power plants, Hg⁰ is difficult oxidized to Hg²⁺ [14,15]. Therefore, to simultaneously remove NO_x and Hg⁰, the low-temperature deNO_x technology along with Hg⁰ capture needs to be improved.

In previous studies, low-temperature NH₃-SCR technology had been widely studied and appears to be a potential method for NO removal. Many transition metal oxides such as MnO_x, FeO_x, V₂O₅, and CoO_x have been employed as catalysts for NO removal [16–19]. Mn-based oxides attracted much attention for capturing Hg⁰ due to their high redox potential, low cost and environmental friendliness [20]. The valence state of Mn and the existing state of O are important for the removal of Hg⁰. During the Hg⁰ removal process,

* Corresponding author. Fax: +86 21 54745591.

E-mail address: nqyan@sjtu.edu.cn (N. Yan).

Hg^0 oxidized to Hg^{2+} on the surface of MnO_x , followed by reduction of high valance Mn^{4+} to Mn^{3+} or Mn^{2+} . Then the oxidized mercury exists as $\text{Hg}-\text{O}$ on the surface of the Mn-based materials. Among various Mn-based low-temperature NH_3 -SCR catalysts, perovskite type Mn-based oxides have recently attracted growing interest as alternative catalysts due to their low cost, high catalytic activity and strong thermal stability [21–25]. The general chemical formula for perovskite oxide is ABO_3 , in which the A ions can be rare earth and alkaline ions, and the B ions are often first-row transition metal ions. The catalytic properties are primarily due to the abnormal valence of the B ion, which is induced by the electric neutrality principle. The Mn ions can occupy the B site of perovskite oxides. The abundance of adsorbed oxygen and the oxygen valance may result in Hg^0 oxidation. LaMnO_3 exhibited a higher catalytic oxidation performance than that of other Mn-based perovskite oxides. In addition, LaMnO_3 had been used as low-temperature catalyst for NO removal. However, there was still no attempt for the catalytic oxidation of Hg^0 using NH_3 -SCR catalysts.

Herein, LaMnO_3 perovskite oxides were synthesized for the removal of Hg^0 . A fixed-bed reaction system was constructed to investigate the Hg^0 removal performance. The effects of O_2 , NH_3 , NO , H_2O and SO_2 flue gas components were considered in our study and the mechanism for Hg^0 capture under different gas components is discussed. Furthermore, the mercury desorption performance was also investigated in our study.

2. Experimental

2.1. Catalyst preparation

The LaMnO_3 catalysts were prepared using a sol-gel method. Briefly, the required amount of $\text{La}(\text{NO}_3)_3$ and $\text{Mn}(\text{NO}_3)_3$ was dissolved in diluted water, followed by the addition of citric acid (CA) to the mixture. The temperature of the aqueous solution was maintained at 80 °C. The molar ratio of La:Mn:CA was 1:1:2. After vigorous stirring and evaporation, a transparent gel was formed, which was dried at 100 °C overnight. The obtained precursor was calcined at 300 °C for 1 h in air to completely decompose citric acid followed by calcination at 750 °C for 5 h at a rate of 10 °C/min. For comparison, MnO_x and LaO_x were also synthesized according to the same sol-gel method.

2.2. Physical characterization

The materials were characterized and analyzed using various techniques. The crystallinity of the fresh samples were determined by X-ray diffraction (XRD, APLX-DUO, BRUKER, Germany) on with Cu-K α radiation. The XRD patterns were recorded in a 2 θ range from 10° to 80° at a scanning rate of 5°/min. The multipoint Brunauer–Emmett–Teller (BET) surface was analyzed using a N_2 sorption measurement (Nova-2200 e) at 77 K. The pore diameter and pore volume were calculated based on the Barrett–Joyner–Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS, Shimadzu–Kratos) was used to examine the valance states of the elements on the surface of the materials. This instrument coupled with an ultra DLD spectrometer with an Al K α excitation source. The C 1s line at 284.6 eV was employed as a reference for the binding energy calibration. The morphology and structure of as-prepared materials were observed via a transmission electron microscopy (TEM), and the images were using a JEOLJEM-2010 TEM electron microscope operating at 200 kV. The reducibility of the samples was determined using H_2 -TPR experiments, and these experiments were performed on a Chemisorp TPX 290 instrument. The samples were degassed at 200 °C for 3 h under

an Ar atmosphere prior to the tests, and the reducing gas consisted of 10% H_2/Ar .

$\text{NH}_3 + \text{O}_2$ and $\text{NO} + \text{O}_2$ -temperature programmed desorption ($\text{NH}_3 + \text{O}_2$ -TPD and $\text{NO} + \text{O}_2$ -TPD) was performed using the fixed-bed adsorption system shown in Fig. 1. A FT-IR gas analyzer was employed to detect the gas components along with the increase in temperature. 20 mg of each sample was pre-treated by 500 ppm $\text{NH}_3 + 4\%$ O_2 (for $\text{NH}_3 + \text{O}_2$ -TPD) and 500 ppm $\text{NO} + 4\%$ O_2 (for $\text{NO} + \text{O}_2$ -TPD) at 50 °C, until the NH_3 or NO concentration did no change. $\text{NH}_3 + \text{O}_2$ and $\text{NO} + \text{O}_2$ were balanced with pure N_2 (total flow rate = 500 ml/min). Then, the fixed-bed temperature was increased at a rate of 10 °C/min and NO , NH_3 , N_2O and NO_2 were detected and recorded using a FT-IR gas analyzer.

2.3. Hg^0 removal tests

The Hg^0 removal activities were evaluated using a fixed-bed reactor, and a schematic representation of the Hg^0 adsorption system is shown in Fig. 1. An Hg^0 permeation tube was used to generate Hg^0 vapor carried by pure N_2 , which was introduced to the inlet of the gas mixer. Other gases including NO , O_2 , SO_2 , and H_2O vapor were introduced to the gas mixer at constant flow rates. NH_3 was separately introduced into the simulated flue gas. The flow rate was controlled by mass flow controllers (MFC) and the total flow rate was set to 200–500 ml/min. A fixed-bed reactor system was used to investigate the Hg^0 adsorption performance. The reaction temperature was controlled from 50 to 350 °C by a temperature controller tubular furnace. A cold vapor atomic absorption spectroscopy (CVASS) analyzer was employed as an online continuous detector that could only detect Hg^0 . The concentration of Hg^0 was measured using Lumex RA 915+. The inlet concentration of Hg^0 was 100–500 $\mu\text{g}/\text{m}^3$. At the beginning of each test, the simulated gas bypassed the reactor and the inlet gas was detected to ensure a stable Hg^0 concentration. Then the simulated gas passed the samples and the Hg^0 concentration was detected by CVASS online system.

The Hg^0 removal efficiency and adsorption capacities were calculated according to Eqs. (1) and (2):

$$\eta = \frac{\text{Hg}_{\text{in}}^0 - \text{Hg}_{\text{out}}^0}{\text{Hg}_{\text{in}}^0} \quad (1)$$

$$Q = \frac{1}{m} \int_{t_2}^{t_1} \left(\frac{\text{Hg}_{\text{in}}^0 - \text{Hg}_{\text{out}}^0}{\text{Hg}_{\text{in}}^0} \right) \times f \times dt \quad (2)$$

$$\text{NO removal efficiency} = \frac{\text{NO}_{\text{in}} - \text{NO}_{\text{out}}}{\text{NO}_{\text{in}}} \quad (3)$$

where η is the Hg^0 removal efficiency, Hg_{in}^0 is the inlet concentration of Hg^0 , Hg_{out}^0 is the outlet concentration of Hg^0 , Q is the Hg^0 adsorption capacity, m is the mass of the sorbent in the fixed-bed, f is the flow rate of the influent, and t_0 and t_1 are the initial and final test times, respectively, of the breakthrough curves.

2.4. NH_3 -SCR catalytic activity measurement

The NH_3 -SCR experiments were also performed in a fixed bed system. The experiments were performed according to the procedures employed in the Hg^0 adsorption tests. 20 mg sample was inserted into the reactor under an atmosphere consisting of 500 ppm NH_3 , 500 ppm NO and 4% O_2 , which was balanced by N_2 , at a total flow rate of 500 ml/min. The temperature ranged from 100 to 300 °C. The FT-IR gas analyzer was employed to detect the gas component in the outlet of the flue gas.

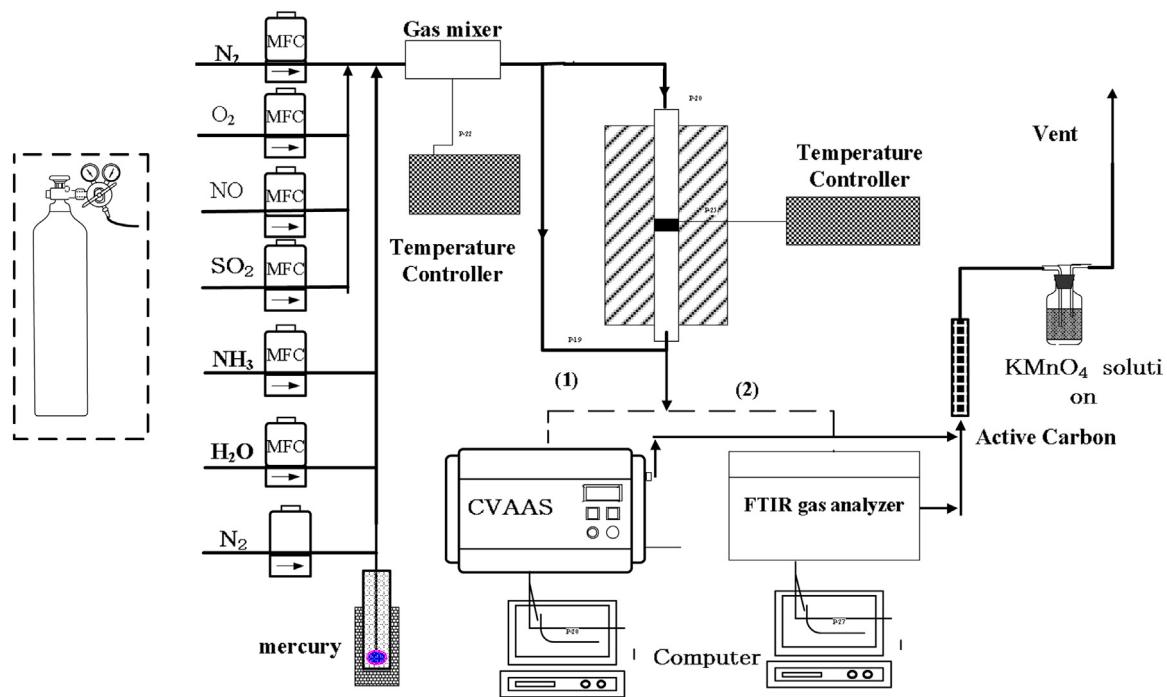


Fig. 1. Flow process of Hg⁰ adsorption and the NH₃-SCR assessment system.

2.5. Regeneration measurement

The mercury temperature programmed desorption (Hg-TPD) method was developed to evaluate the desorption performance of LaMnO₃. Prior to each test, the sorbents were adsorbed for 20 min at 150 °C with N₂ (for N₂ + Hg-TPD), 4% O₂ (for O₂ + Hg-TPD), 4% O₂ + 500 ppm NH₃ (for O₂ + NH₃ + Hg-TPD), 4% O₂ + 500 ppm NO (for O₂ + NO + Hg-TPD) and 4% O₂ + 500 ppm SO₂ (for O₂ + SO₂ + Hg-TPD). After the furnace cooled to 100 °C, the sorbents were regenerated by heating from 100 to 700 °C in a pure N₂ carrier gas. The heating rates were set to 2, 5 and 10 °C/min. The mercury signal was recorded by a CVASS online system.

3. Results and discussion

3.1. Physicochemical properties

Fig. 2 shows the XRD patterns of the LaO_x, MnO_x and LaMnO₃ samples. For the LaO_x samples, the peaks were assigned to the La(OH)₃ diffraction pattern (JCPDS 83-2034) and La₂O₃ diffraction pattern (JCPDS 05-0602) [26]. For MnO_x, Mn₂O₃ (JCPDS 24-0508) was the primary phase, and only a few peaks were ascribed to other crystalline manganese oxides. However, for LaMnO₃, the peaks were located at 22.8, 32.6, 40.2, 46.7, 52.8, 58.1, 68.3 and 77.8°, and all of these characteristic peaks can be well indexed to a perovskite phase (PDF-88-0633) with a rhombohedral structure.

The N₂ adsorption-desorption isotherms and pore size distributions of LaMnO₃ were investigated, and the results are shown in Table 1. The BET surface area of the prepared LaMnO₃ was

16.6 m²/g, and the total pore volume and average pore diameter were 0.118 cm³/g and 11.5 nm, respectively. For comparison, the BET surface areas of La₂O₃ and MnO_x were also calculated. The BET surface area of La₂O₃ was 2.3 m²/g, which was smaller than that of LaMnO₃, and the pore volume was 0.068 cm³/g, which was also smaller than that of LaMnO₃. For MnO_x, the BET surface area was 11.2 m²/g, and the pore volume and pore diameter were 0.051 cm³/g and 3.308 nm, respectively. To further elucidate the textural properties of LaMnO₃, the TEM image is shown in Fig. S1, the uniform crystal lattice was indicative of the perovskite structure. In addition, the EDS analysis indicated that the elemental components were La, Mn and O.

Nest, the valance states of the elements were characterized by XPS. The results are reported in Fig. 3(a). For the Mn 2 p spectrum of LaMnO₃, the peaks at 643.7 and 641.7 eV were correspond to Mn⁴⁺ and Mn³⁺, respectively [27]. The ratio of Mn⁴⁺/Mn³⁺ was determined to be 33.93/66.07. A higher valence state of Mn may result in a higher catalytic oxidation activity [28,29]. The state of O was also evaluated by XPS analysis, as shown in Fig. 3B, in the O 1s spectrum of LaMnO₃, the peaks located at 531.0 and 529.6 eV were ascribed to the lattice oxygen (O_{latt}) and adsorbed oxygen (O_{ads}), respectively [30]. The ratio of O_{latt}/O_{ads} was approximately 47.51/52.49 in the fresh samples. The adsorbed oxygen was favorable for Hg⁰ capture [29,31].

3.2. Hg⁰ removal over NH₃-SCR LaMnO₃ perovskite oxide

3.2.1. NH₃-SCR performance over LaMnO₃

LaMnO₃ has been previously used as a low-temperature NH₃-SCR catalyst for NO removal from coal-fired flue gas [32]. As shown in Fig. 4(a), the NH₃-SCR performance of LaO_x, MnO_x and LaMnO₃ were tested. LaO_x exhibited almost no activity for NO removal. MnO_x exhibited a NO conversion of approximately 20% at 250 °C. However, for LaMnO₃, the NO conversion was higher than 65% at 200 °C. When the temperature increased from 250 to 350 °C, the NO conversion efficiency decreased. The Mn-based materials lost their activity for NO conversion at higher temperature (>200 °C). This

Table 1

Textural properties (BET surface area, pore volume and pore diameter) of the as-prepared samples.

Materials	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)
La ₂ O ₃	2.3	0.068	3.34
MnO _x	11.2	0.051	3.30
LaMnO ₃	16.6	0.118	11.5

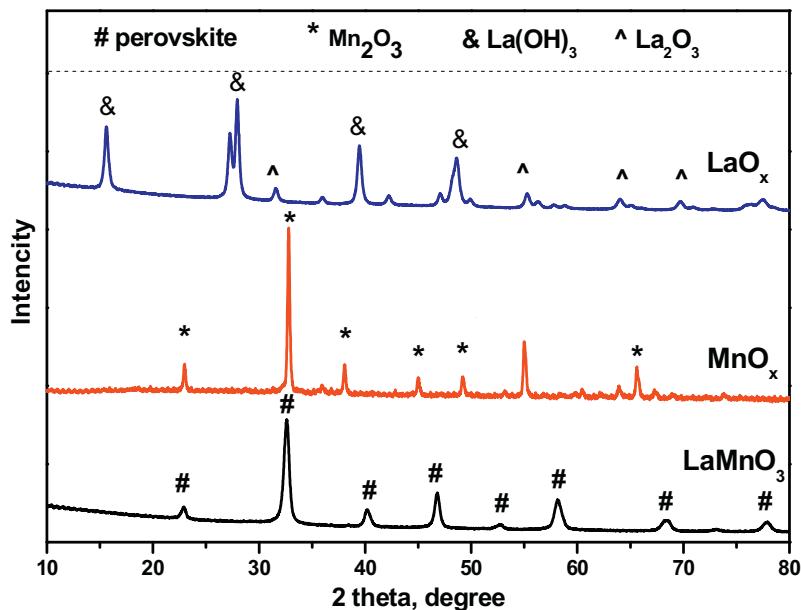


Fig. 2. XRD patterns of the LaO_x , MnO_x and LaMnO_3 samples.

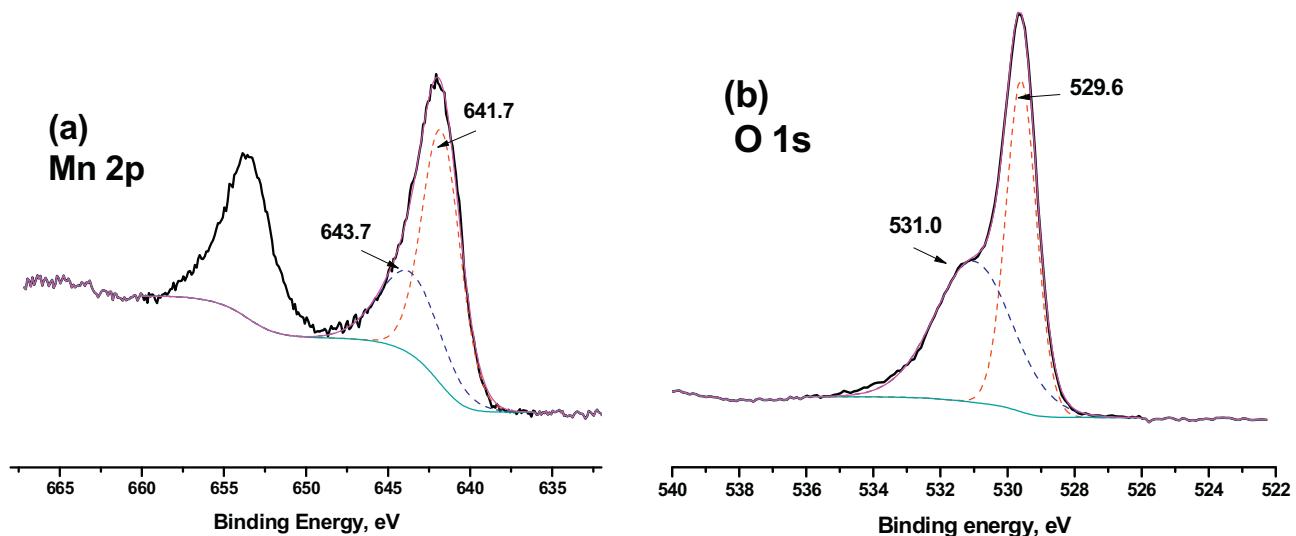


Fig. 3. XPS spectra of fresh LaMnO_3 over the spectral regions of (a) Mn 2p and (b) O 1s.

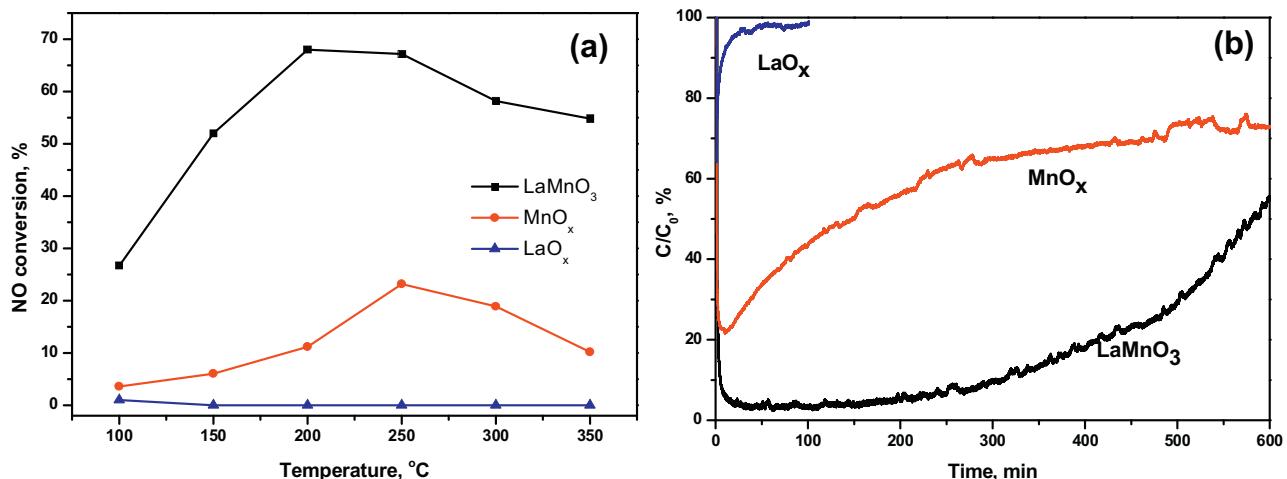


Fig. 4. Performance of (a) NO conversion and (b) Hg^0 removal over LaO_x , MnO_x and LaMnO_3 ; Reaction condition: GHSV = 478,000 h⁻¹ and 4% O₂.

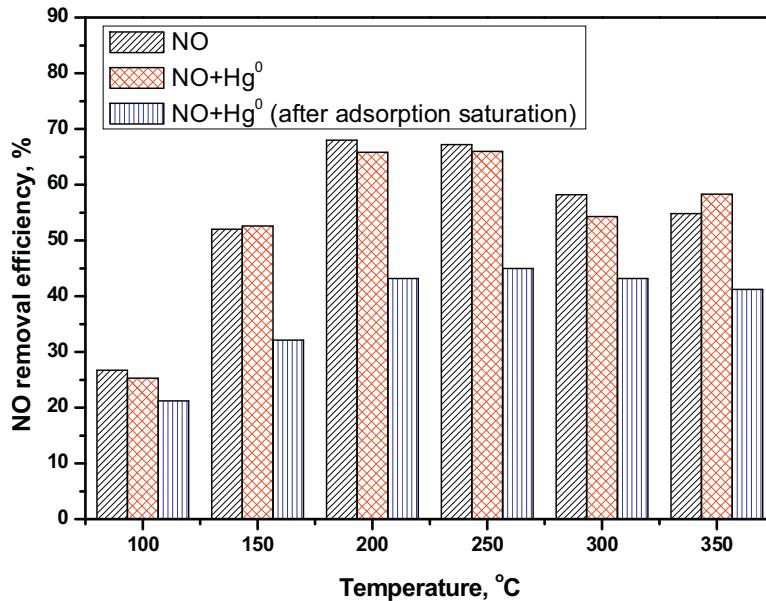


Fig. 5. The effect of Hg⁰ on NO removal efficiency. (Reaction conditions: NO = NH₃ = 500 ppm, Hg⁰ = 500 µg/m³, O₂ = 4%, GHSV = 478,000 h⁻¹ and N₂ as balance.).

temperature window (100–200 °C), it is beneficial for Hg⁰ capture downstream from ESP or FF in the coal-fired power plants.

3.2.2. Hg⁰ adsorption activity over LaMnO₃

To investigate the role of the perovskite crystal structure on Hg⁰ removal, the adsorption test was performed in a fix-bed adsorption system. As shown in Fig. 4(b), Hg⁰ removal activity increased in the following order: LaO_x < MnO_x < LaMnO_x. LaO_x oxide exhibited almost no activity for Hg⁰ removal. MnO_x gradually lost its Hg⁰ removal ability, and the Hg⁰ removal efficiency was only approximately 30% after 600 min reaction. LaMnO₃ achieved the best performance with a Hg⁰ removal efficiency that was higher than 85% after 600 min reaction. The saturation adsorption capacity of LaMnO₃ for Hg⁰ was calculated to be approximately 7.65 mg/g. The effect of Hg⁰ on NO removal was also investigated. As shown in Fig. 5, in the presence of Hg⁰, it existed a slight decrease for the removal of NO. But the trend was similar. It indicated that the addition of Hg⁰ in the simulated gas had little effect on the NO removal. To further confirm the NO removal performance, the sample was first used for Hg⁰ adsorption, and after adsorption saturation, the sample was used for NO removal. The NO removal efficiencies decreased sharply, especially at low temperature. Mn is most likely the main active site for Hg⁰ removal based on previous reported results [29,31,33]. The high activity of LaMnO₃ was due to the benefit of perovskite crystal structure [34]. Mnⁿ⁺ exhibited a better dispersion in the perovskite structure where it was located in the B sites of the lattice. The highly dispersed Mnⁿ⁺ was beneficial for the Hg⁰ catalytic oxidation on its surface [34]. Based on the characterization results, LaMnO₃ had the largest BET surface area, which was approximately 50% larger than that of MnO_x. The larger surface area was beneficial for physical adsorption. However, the large surface area was not the primary reason for the higher Hg⁰ removal efficiencies. In our previous studies, the BET surface areas of Mn-based materials were larger than LaMnO₃ [35,36]. Therefore, the perovskite structure of LaMnO₃ contributed to the high catalytic activity for Hg⁰ removal.

The effects of the Hg⁰ initial concentration, gas hourly space velocity (GHSV) and temperature were investigated. As shown in Fig. 6(a), the initial Hg⁰ concentrations were set to 100, 300 and 500 µg/m³, respectively. When the initial Hg⁰ concentration was 500 µg/m³, the Hg⁰ removal efficiency was approximately 50%

after 600 min adsorption. However, when the initial Hg⁰ concentration decreased to 300 µg/m³, the Hg⁰ removal efficiency was higher than that at an initial Hg⁰ concentration of 500 µg/m³ after 600 min adsorption. When the initial Hg⁰ concentration was further decreased to 100 µg/m³, the removal efficiency was maintained at a value higher than 95%. The effect of the GHSV was also investigated. The GHSV was set by changing the total gas flow rate. The GHVs were 478,000, 286,800 and 95,600 h⁻¹ when the total flow rates were 500, 300 and 100 ml/min, respectively. As shown in Fig. 6(b), the Hg⁰ removal efficiency increased when the GHSV decreased. The Hg⁰ removal efficiency (after 600 min adsorption) was approximately 90% when the GHSV decreased to 95,600 h⁻¹. To further investigate the Hg⁰ removal mechanism over LaMnO₃ and the effects of the gas components, the reaction conditions were set to 500 µg/m³ of inlet Hg⁰ and GHSV = 478,000 h⁻¹ even though the removal efficiency was not high under this condition. The effect of temperature was also investigated, and the temperature window ranged from 100 to 300 °C. The Hg⁰ capacities increased from 6.13 mg/g at 100 °C to 6.22 mg/g at 150 °C. However, when the temperature increased from 150 to 300 °C, the Hg⁰ capacity decreased to only 3.01 mg/g at 300 °C. The higher temperature resulted in LaMnO₃ losing its performance for Hg⁰ removal. Manganese oxides may exhibit better activity at low temperature [35,37]. Herein, to gain insight into the LaMnO₃ sorbents, the reaction temperature were set to 150 °C, the inlet concentration was 500 µg/m³ and the GHSV was 478,000 h⁻¹.

3.2.3. Effect of O₂ on Hg⁰ adsorption

In general, the Hg⁰ removal mechanism over Mn-based oxides involves the chemical adsorption. The catalytic oxidation of Hg⁰ to Hg²⁺ enhanced the performance for Hg⁰ capture. O₂ is the common oxidants of Hg⁰ oxidation. Pure physical adsorption does not result in higher Hg⁰ capacities. The adsorption experiments under pure N₂ were performed, and the results are shown in Fig. 7. LaMnO₃ exhibited a gradual decrease in its Hg⁰ removal performance. After 125 min adsorption, the Hg⁰ removal efficiency was only 50%. However, when 4% O₂ was added to the simulated gas, the Hg⁰ removal efficiency increased. The existence of O₂ in the flue gas participated in the Hg⁰ removal process. The Hg⁰ removal experiments under pure N₂, 4% O₂ and 8% O₂ during a 600 min reaction were further investigated. The Hg⁰ adsorption capacities were calculated and are

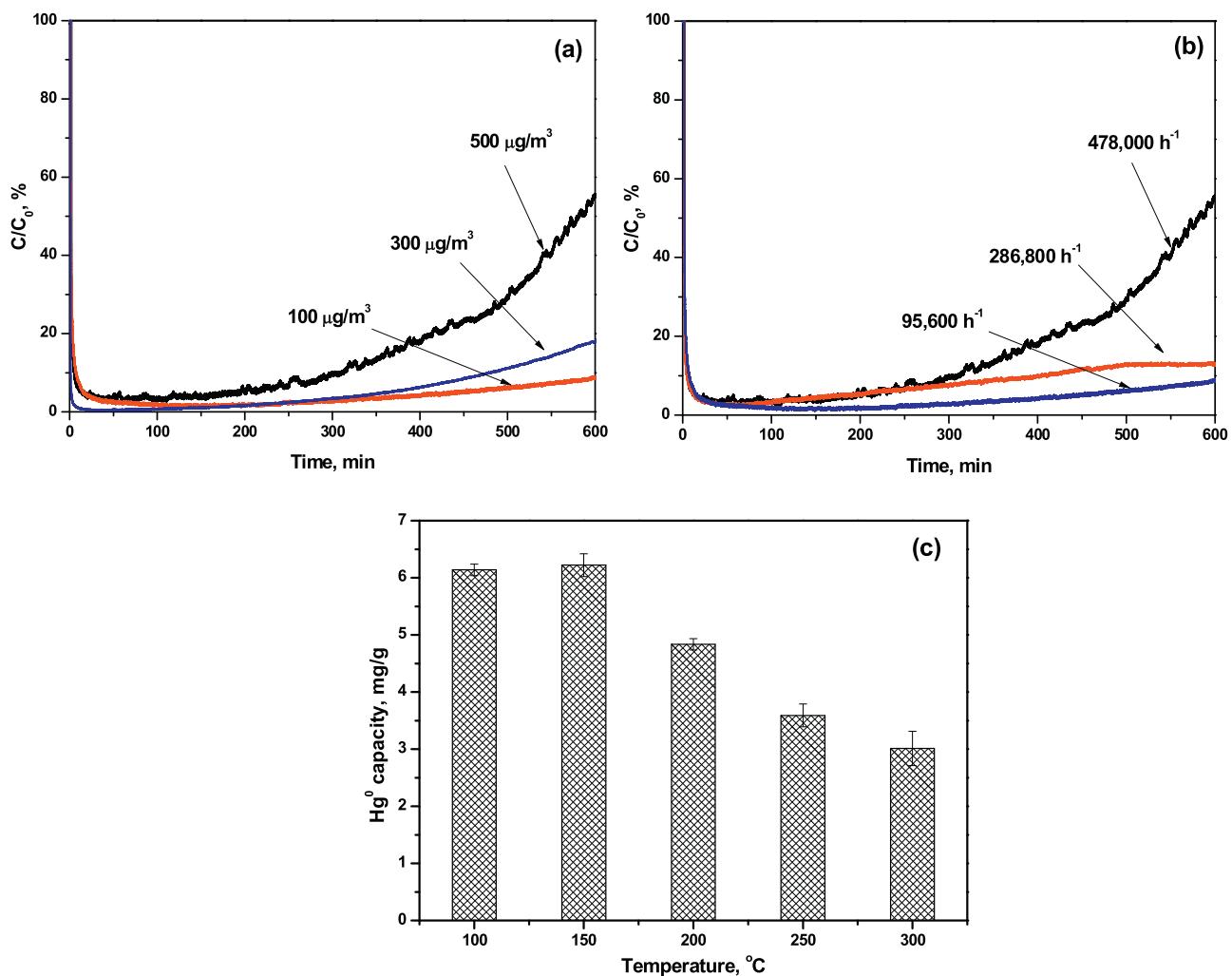


Fig. 6. (a) Effect of initial Hg^0 concentration, (b) gas hourly space velocity (GHSV), and (c) temperature on Hg^0 adsorption over LaMnO_3 . Reaction condition: 4% O_2 .

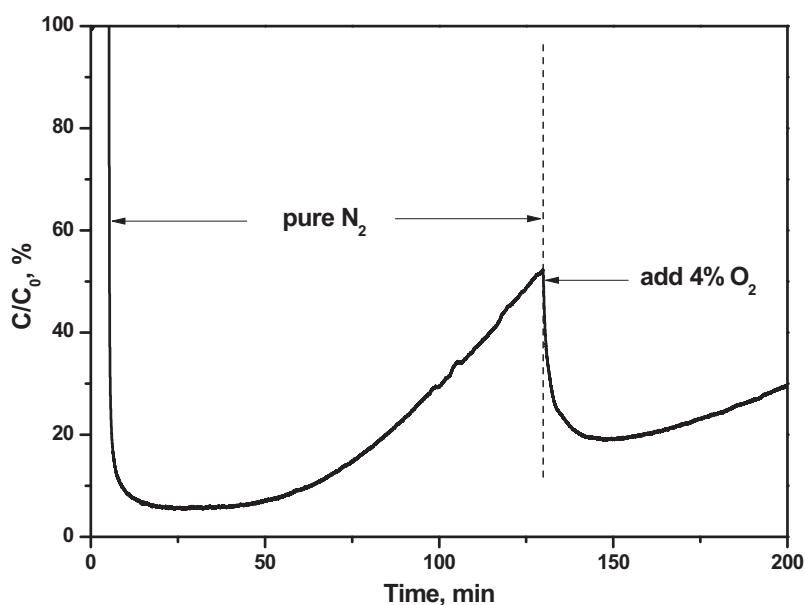


Fig. 7. Effect of O_2 on Hg^0 removal. Reaction condition: 150 °C; GHSV = 478,000 h^{-1} ; 4% O_2 .

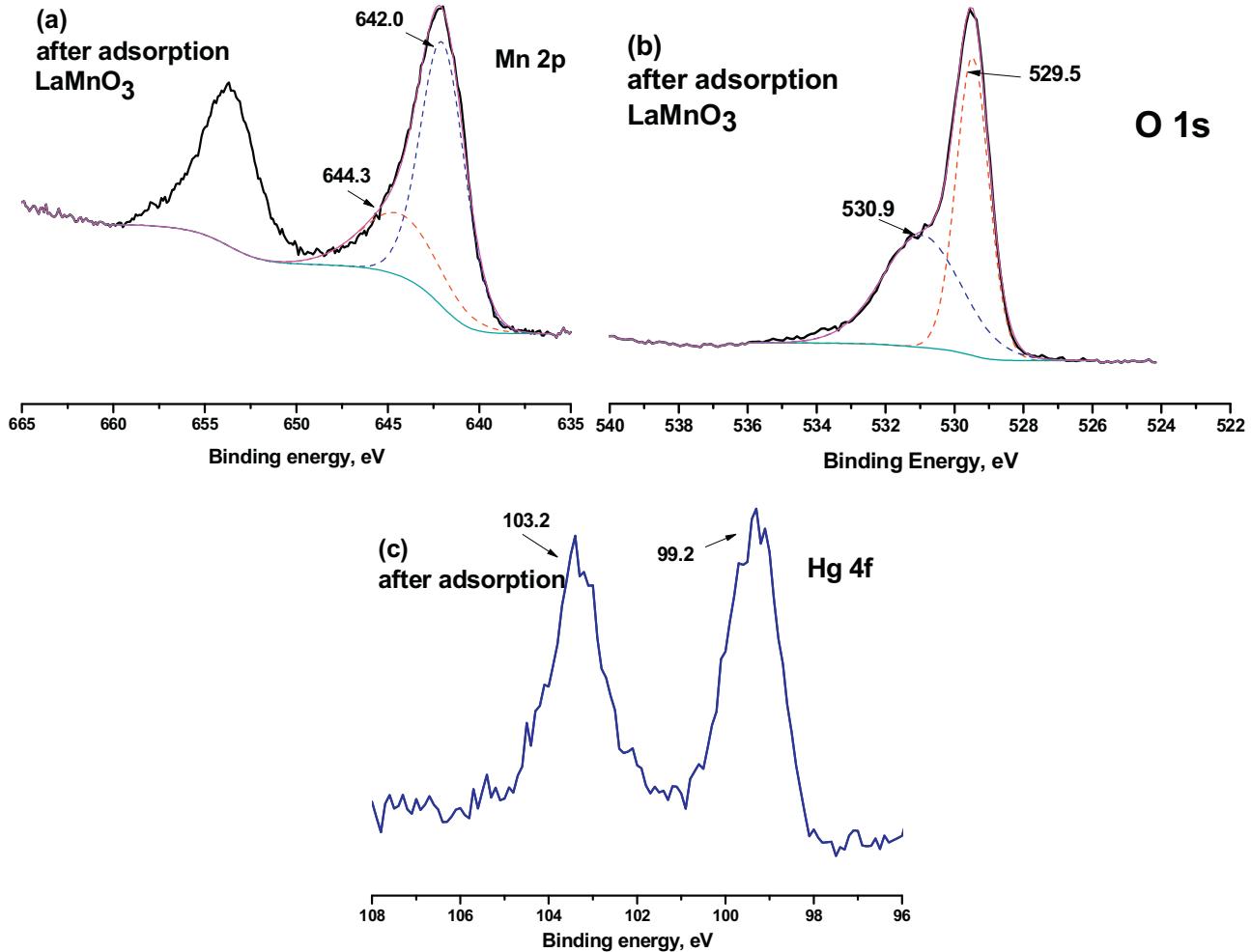


Fig. 8. XPS spectra of the LaMnO₃ sample after adsorption: (a) Mn 2p, (b) O 1s and (c) Hg 4f.

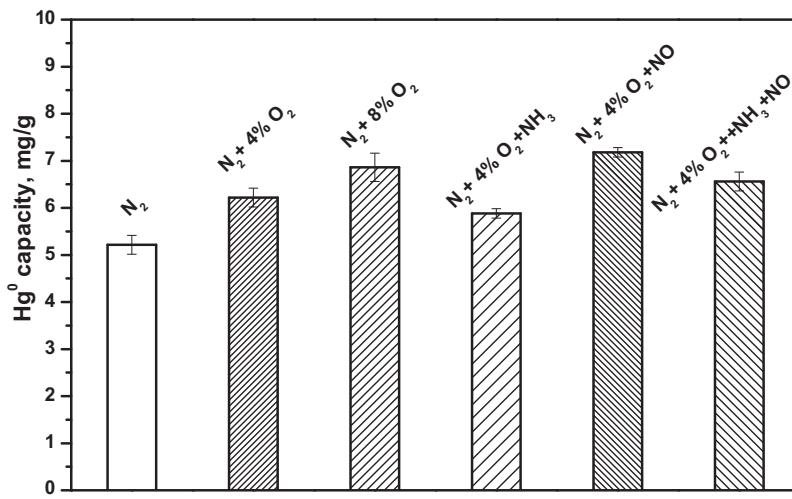


Fig. 9. Hg⁰ capacities under pure N₂, 4% O₂, 8% O₂, 4% O₂ + 500 ppm NH₃, 4% O₂ + 500 ppm NO, and 4% O₂ + 500 ppm NO + 500 ppm NH₃. Reaction condition: 150 °C and GHSV = 478000 h⁻¹.

shown in Fig. 9, the Hg⁰ capacity decreased by approximately 17% in the absence of O₂. When the concentration of O₂ was increased to 8%, the Hg⁰ capacities increased from 6.2 mg/g to approximately 6.8 mg/g. The H₂-TPR profile of LaMnO₃ is shown in Fig. S2. The peaks centered at 330.5 (peak 1) and 741.1 °C (peak 2) were due

to the reduction of Mn⁴⁺ to Mn³⁺ and Mn³⁺ to Mn²⁺, respectively. The peak 1/peak 2 ratio was 56.8/43.2. The results indicated the boundaries between Mn⁴⁺ to Mn³⁺ and Mn³⁺ to Mn²⁺.

After adsorption, the XPS spectra of Mn 2p, O 1s and Hg 4f were recorded, and the results are shown in Fig. 8. In the XPS spec-

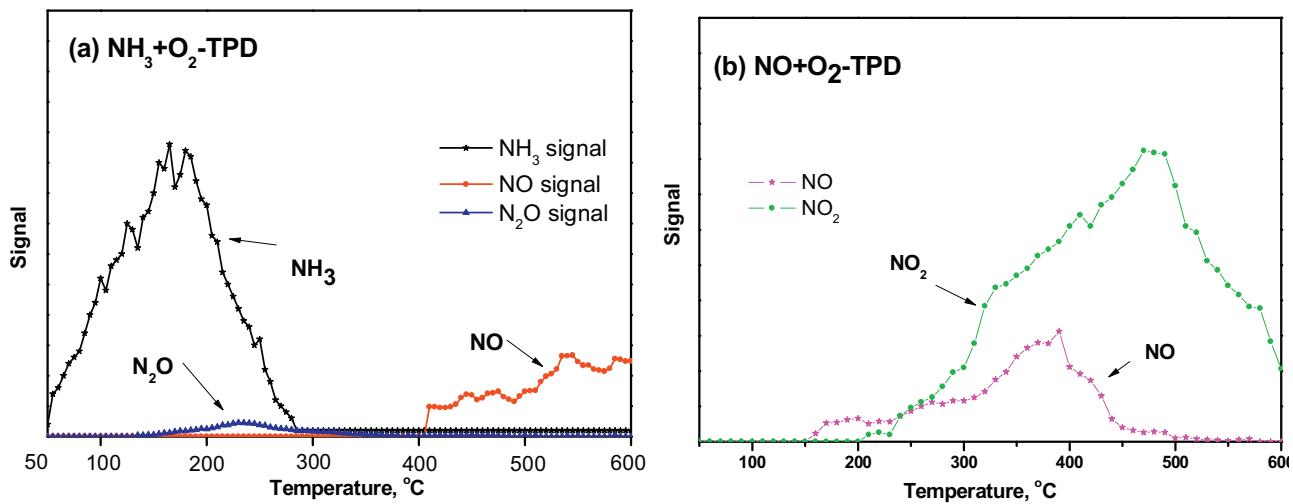
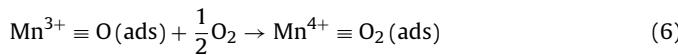
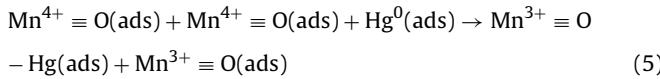


Fig. 10. (a) NH₃ + O₂-TPD, and (b) NO + O₂-TPD profiles over the LaMnO₃ samples.

tra of Mn 2p shown in Fig. 8(a), the Mn⁴⁺/Mn³⁺ ratio changed to 29.14/70.86. A portion of the Mn⁴⁺ changed to Mn³⁺ during the adsorption process. After adsorption, (Fig. 8(b)), the O_{latt}/O_{ads} ratio was approximately 48.05/51.05, and the ratio decreased due to an increase in O_{ads} on the surface of LaMnO₃. The oxygen in the flue gas was first adsorbed on the surface of LaMnO₃ to generate O_{ads}. This O_{ads} combined with Hg⁰ which was also adsorbed on the surface of LaMnO₃. To further confirm the results, the XPS spectrum of Hg 4f is shown in Fig. 8(c), and the peaks located at 103.2 and 99.2 eV were ascribed to HgO. The adsorbed Hg⁰ existed as HgO on the surface of LaMnO₃. The mechanism of Hg⁰ adsorption can be illustrated as follows:



3.2.4. Effect of NH₃ and NO on Hg⁰ removal

LaMnO₃ was used as the low temperature NH₃-SCR catalyst in previous studies. As shown in Fig. 9, the effects of NH₃ and NO on the Hg⁰ adsorption capacities was presented. The reaction condition were 500 ppm NH₃, 500 ppm NO, 150 °C and a GHSV = 478000 h⁻¹. NH₃ decreased the Hg⁰ capacity of LaMnO₃, and the Hg⁰ capacities decreased to 5.88 mg/g compared to 6.22 mg/g only under only 4% O₂. However, NO enhanced the Hg⁰ adsorption capacity, and the Hg⁰ capacity was 7.18 mg/g after 600 min of adsorption. When the gas component was 4% O₂ + 500 ppm NO + 500 ppm NH₃, the Hg⁰ capacity decreased compared to that with 4% O₂ + 500 ppm NO and increased compared to that with 4% O₂ + 500 ppm NH₃.

To investigate the NH₃ surface oxidation and NO oxidation performance, NH₃ + O₂-TPD and NO + O₂-TPD was performed in our study. A FT-IR gas analyzer was employed to detect the gas component along with the increase of temperature. As shown in Fig. 10(a), when the temperature increased from 50 °C, the adsorbed NH₃ started to release from the surface of LaMnO₃, and this NH₃ was due to the physical-adsorbed NH₃ (ad-NH₃) on the LaMnO₃ surface. At a temperature of 150 °C, N₂O was detected. As the temperature increased to 400 °C, NO was released from the LaMnO₃ surface. The ad-NH₃ may be oxidized to N₂O at low temperatures and NO at higher temperatures. The NO + O₂-TPD was also investigated

in this study. As shown in Fig. 10(b), the adsorbed-NO (ad-NO) started to desorb from the surface of LaMnO₃ at 150 °C. As the temperature increased to 200 °C, NO₂ started to release. The ad-NO was most likely oxidized to NO₂ by catalytic oxidation over LaMnO₃. The mechanism of NH₃-SCR reaction over LaMnO₃ has been previously reported, especially for the reaction following the L-H mechanism [32,34]. It is unnecessary to distinguish the species on the LaMnO₃ surface after NH₃/NO adsorption in previous studies based on DRIFTS studies. The desorbed NH₃ can be assigned as ad-NH₃, and the desorbed NO can be assigned to NH₃ bond to acid sites [34]. Therefore, ad-NH₃ formed NH₄⁺ on the surface covered the active sites and consumed surface oxygen, which inhibited Hg⁰ oxidation, resulting in a low removal efficiency. However, the ad-NO formed NO₂ on the surface of LaMnO₃, and these species are most likely responsible for Hg⁰ oxidation [38].

3.2.5. Effect of SO₂ and H₂ on Hg⁰ removal

The effects of SO₂ and H₂O on Hg⁰ removal were also investigated (Fig. 11). SO₂ had an adverse effect on the Hg⁰ removal, and Hg⁰ capacity decreased approximately 20% when 500 ppm SO₂ was included in the simulated gas. SO₂ may easily react with Mn-based materials to form Mn-SO₄²⁻ [38,39]. NH₃ resulted in a decrease in the Hg⁰ capacity when SO₂ was present, but NO promoted Hg⁰ removal even when SO₂ was included in the simulated gas. NH₃ can react with SO₂ to form sulfate species, and causes catalyst deactivation. However, the existence of H₂O had an adverse effect on Hg⁰ adsorption, especially when NH₃ and NO co-existed. Therefore, NO may form nitrate which results in a loss in oxidation performance. Furthermore, the active sites of LaMnO₃ were occupied, resulting in low adsorption capacities. Moreover, the presence of both SO₂ and H₂O had a serious adverse effect on Hg⁰ removal over LaMnO₃, and the Hg⁰ capacity was only 50% compare to that under N₂ + 4%O₂. When NH₃ and NO were added to the simulated gas, the Hg⁰ adsorption capacity further decreased, and the capacity decreased to only 2.5 mg/g under 4% O₂ + 4% H₂O + 500 ppm NH₃ + 500 ppm NO + 500 ppm SO₂. It is interesting to further discuss the mechanism for the interaction among the H₂O, NH₃ and NO (Fig. 11).

3.3. Mercury temperature-programmed-desorption (Hg-TPD)

The mercury temperature-programmed-desorption (Hg-TPD) method was performed. In addition, the desorption activation energy (E_d) was calculated to explain the binding force between mercury and LaMnO₃. The adsorption under different gas atmo-

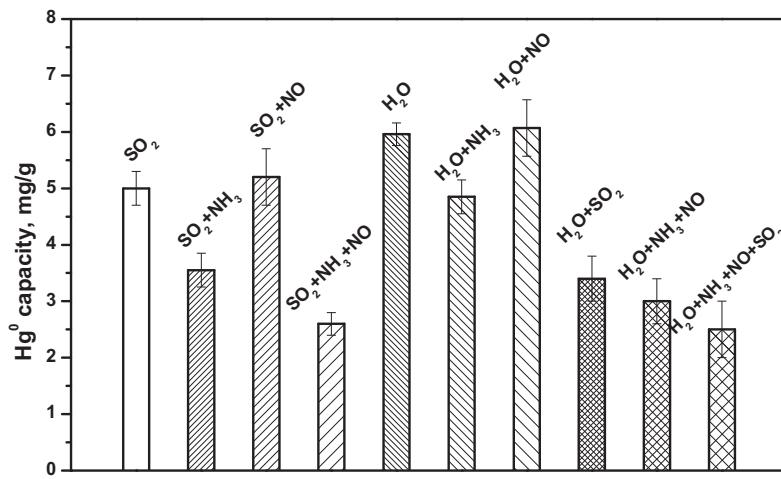


Fig. 11. Effects of SO₂ and H₂O on the Hg⁰ adsorption capacity. Reaction condition: 150 °C; GHSV = 478,000 h⁻¹; O₂: 4%; NH₃: 500 ppm; NO: 500 ppm; SO₂: 500 ppm; H₂O: 4%.

sphere and desorption under pure N₂ was first studied. The Hg-TPD model for the E_d calculation was as follows:

The Hg⁰ desorption process was assumed as to follow first-order kinetics [40–42]:

$$\frac{r_d}{N_s} = -\frac{d\theta}{dt} = k_d \theta \quad (7)$$

where r_d is the desorption rate of mercury from the sorbent (mol/min), N_s is the maximum mercury concentration on the unit surface of the sorbent (mol/cm²), θ is the transient coverage of mercury, t is the time (min) and k_d is the desorption rate.

Based on Eq. (7), the related parameters can be defined as follows:

$$k_d = A \exp\left(-\frac{E_d}{RT}\right) \quad (8)$$

$$\frac{r_d}{N_s} = -\frac{d\theta}{dt} = A \theta \exp\left(-\frac{E_d}{RT}\right) \quad (9)$$

$$T = T_0 + \beta t \quad (10)$$

where R is the gas constant, T is the temperature, A is the pre-exponential factor, β (K/min) is the heating rate and T_0 (K) is the initial temperature of TPD experiment. Assuming that the desorption rate reaches a maximum value at a certain temperature T_p (K), then $dr_d/dt = 0$, and Eq. (7) can be expressed as follows:

$$2\ln T - \ln \beta = \frac{E_d}{RT_p} + \ln \frac{E_d}{AR} \quad (11)$$

Based on Eq. (11), the Hg-TPD curves under different heating rates are created by plotting of $(2\ln T_p - \ln \beta)$ as a function of $1/T_p$, which generates a linear relationship, and E_d can be calculated.

First, the Hg-TPD experiments were performed using different gas components. N₂ + Hg-TPD, O₂ + Hg-TPD, NH₃ + O₂ + Hg-TPD, NO + O₂ + Hg-TPD and SO₂ + O₂ + Hg-TPD were tested. As shown in Fig. 12, the adsorption under pure N₂ resulted in two peaks. One peak located at approximately 248.5 °C was due to physical-adsorption on the LaMnO₃ surface. The primary desorption peak at approximately 342.5 °C may be associated with chemical-adsorption. For adsorption under 4% O₂, the desorption peak was located at 361.5 °C which is higher than the second peak under N₂. Based on Equation (8), as the desorption temperature increased, the desorption energy increased. For adsorption under NH₃ + O₂ and NO + O₂, the primary desorption peaks were centered at 345.5 and 356.5 °C, respectively. The desorption peaks under O₂, NH₃ + O₂ and NO + O₂ adsorption atmosphere were similar. However, for adsorption under SO₂ + O₂, desorption began at approximately 230 °C,

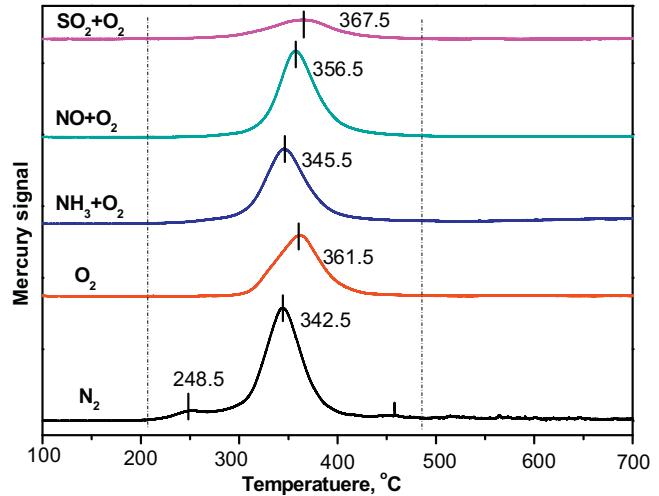


Fig. 12. Hg-TPD curves for LaMnO₃ under different adsorption conditions.

which is lower than that of under an O₂ atmosphere. In addition, a wide peak was observed in the curve of under SO₂ + O₂. The sulfate (SO₄²⁻) on LaMnO₃ surface may have affected the Hg-O binding energy. The desorption energy based on Eq. (8) was calculated, and the O₂ + Hg-TPD for a desorption rate of 2, 5 and 10 °C/min is shown in Fig. S3. The desorption activation energy was 150.50 kJ/mol. LaMnO₃ can be regenerated by thermal desorption. The sample was re-used for Hg⁰ adsorption, as shown in Fig. S4, and the Hg⁰ capacities were nearly the same after the 5th adsorption run. The results indicated that LaMnO₃ can be fully regenerated.

Based on these results, the optimal reaction temperature for NO conversion is 200–250 °C and Hg⁰ adsorption is 100–150 °C. In coal-fired power plants, the catalyst can be used downstream of ESP/FF, and in this section, the temperature is approximately 200 °C. A low-temperature NH₃-SCR catalyst was also used in this section. LaMnO₃ had a NO removal efficiency of approximately 60–70% and a higher Hg⁰ capacity. In a traditional coal-fired power plant, the NO concentration decreases after the SCR reaction, and the Hg⁰ concentration also decreased after the SCR catalyst and ESP/FF. Therefore, the low-temperature NH₃-SCR reactor may also be beneficial for simultaneous removal of Hg⁰ and NO.

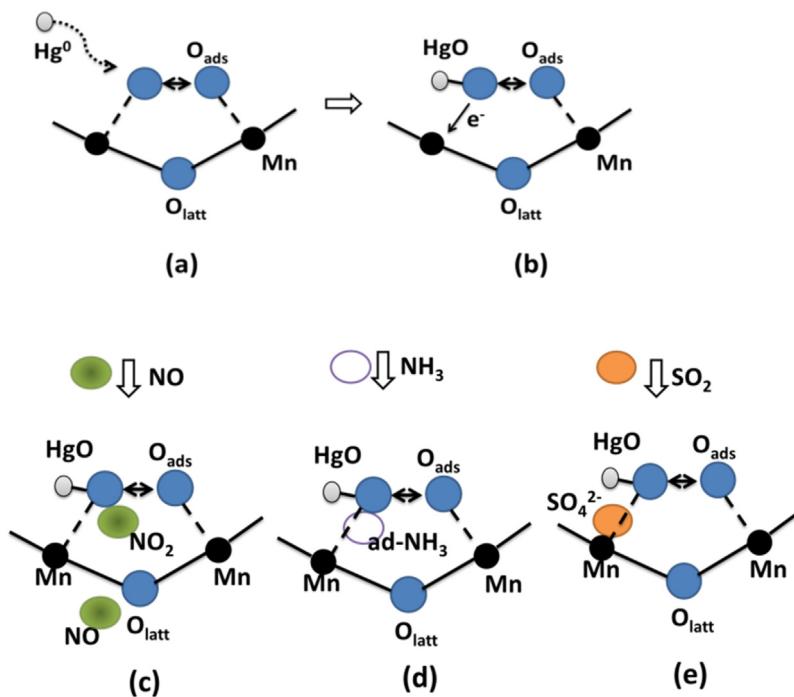


Fig. 13. Proposed reaction mechanism for Hg^0 adsorption under different gas compositions over LaMnO_3 .

4. Conclusions

In this study, LaMnO_3 perovskite oxide, which was used as a low-temperature NH_3 -SCR catalyst, was confirmed to be a Hg^0 sorbent. The perovskite structure was beneficial for Hg^0 catalytic oxidation and adsorption, and the reduction of Mn^{4+} to Mn^{3+} results in oxidation of Hg^0 to Hg^{2+} . The adsorbed oxygen combined with Hg^{2+} to form HgO species on the LaMnO_3 surface. The adsorption mechanism is briefly illustrated in Fig. 13, the Hg^0 first adsorbed on LaMnO_3 surface, then Hg^0 was oxidized to Hg^{2+} and existed as HgO species. In addition, the existence of NO enhanced the Hg^0 capacity but the presence of NH_3 inhibited Hg^0 adsorption. NO adsorption on LaMnO_3 may result in the formation of NO_2 , which is favorable for Hg^0 oxidation. However, the existence of ad- NH_3 occupied the adsorbed oxygen, resulting in difficulties with $\text{Hg}-\text{O}$ bonding. The existence of SO_2 also decreased the Hg^0 capacity due to the sulfate generated on the LaMnO_3 surface. A further improvement in the LaMnO_3 materials is currently underway. LaMnO_3 exhibited superior performance for Hg^0 adsorption and is an ideal material for the simultaneous removal of Hg^0 and NO at low-temperatures in coal-fired power plants.

Acknowledgement

This study was supported by the Major State Basic Research Development Program of China (973 Program, No. 2013CB430005), the National Natural Science Foundation of China (No. 51478261 and No. 51278294). Thanks for Shanghai Tongji Gao Tingyao Environmental Science and Technology Development Foundation.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2015.12.042>.

References

- [1] W.H. Schroeder, J. Munthe, *Atmos. Environ.* 32 (1998) 809–822.
- [2] N. Pirrone, P. Costa, J. Pacyna, R. Ferrara, *Atmos. Environ.* 35 (2001) 2997–3006.
- [3] K.-H. Kim, V.K. Mishra, S. Hong, *Atmos. Environ.* 40 (2006) 3281–3293.
- [4] Z.-W. Wang, Z.-S. Chen, D. Ning, X.-S. Zhang, *J. Environ. Sci.* 19 (2007) 176–180.
- [5] D.G. Streets, J. Hao, Y. Wu, J. Jiang, M. Chan, H. Tian, X. Feng, *Atmos. Environ.* 39 (2005) 7789–7806.
- [6] H. Kamata, S.-I. Ueno, T. Naito, A. Yukimura, *Ind. Eng. Chem. Res.* 47 (2008) 8136–8141.
- [7] M. Díaz-Somoano, S. Unterberger, K.R. Hein, *Fuel Proc. Technol.* 88 (2007) 259–263.
- [8] Y. Eom, S.H. Jeon, T.A. Ngo, J. Kim, T.G. Lee, *Catal. Lett.* 121 (2008) 219–225.
- [9] R.D. Vidic, D.P. Siler, *Carbon* 39 (2001) 3–14.
- [10] W. Liu, R.D. Vidic, T.D. Brown, *Environ. Sci. Technol.* 34 (2000) 483–488.
- [11] J. Wo, M. Zhang, X. Cheng, X. Zhong, J. Xu, X. Xu, J. Hazard. Mater. 172 (2009) 1106–1110.
- [12] S.J. Lee, Y.-C. Seo, J. Jurng, T.G. Lee, *Atmos. Environ.* 38 (2004) 4887–4893.
- [13] Z. Shen, J. Ma, Z. Mei, J. Zhang, *J. Environ. Sci.* 22 (2010) 1814–1819.
- [14] M.H. Kim, S.-W. Ham, J.-B. Lee, *Appl. Catal. B: Environ.* 99 (2010) 272–278.
- [15] Y. Li, P.D. Murphy, C.-Y. Wu, K.W. Powers, J.-C. Bonzongo, *Environ. Sci. Technol.* 42 (2008) 5304–5309.
- [16] B. Thirupathi, P.G. Smirniotis, *J. Catal.* 288 (2012) 74–83.
- [17] Y.J. Kim, H.J. Kwon, I. Heo, I.-S. Nam, B.K. Cho, J.W. Choung, M.-S. Cha, G.K. Yeo, *Appl. Catal. B: Environ.* 126 (2012) 9–21.
- [18] J. Li, H. Chang, L. Ma, J. Hao, R.T. Yang, *Catal. Today* 175 (2011) 147–156.
- [19] S. Straube, T. Hahn, H. Koeser, *Appl. Catal. B: Environ.* 79 (2008) 286–295.
- [20] Y. Gao, Z. Zhang, J. Wu, L. Duan, A. Umar, L. Sun, Z. Guo, Q. Wang, *Environ. Sci. Technol.* 47 (2013) 10813–10823.
- [21] Y. Nishihata, J. Mizuki, T. Akao, H. Tanaka, M. Uenishi, M. Kimura, T. Okamoto, N. Hamada, *Nature* 418 (2002) 164–167.
- [22] J. Suntivich, K.J. May, H.A. Gasteiger, J.B. Goodenough, Y. Shao-Horn, *Science* 334 (2011) 1383–1385.
- [23] Y. Teraoka, K. Kanada, S. Kagawa, *Appl. Catal. B-Environ.* 34 (2001) 73–78.
- [24] R. Spinicci, A. Tofanari, M. Faticanti, I. Pettiti, P. Porta, *J. Mol. Catal. A-Chem.* 176 (2001) 247–252.
- [25] C. Tofan, D. Klvana, J. Kirchnerova, *Appl. Catal. B-Environ.* 36 (2002) 311–323.
- [26] B. Tang, J. Ge, C. Wu, L. Zhuo, J. Niu, Z. Chen, Z. Shi, Y. Dong, *Nanotechnology* 15 (2004) 1273.
- [27] J. Chen, M. Shen, X. Wang, G. Qi, J. Wang, W. Li, *Appl. Catal. B: Environ.* 134–135 (2013) 251–257.
- [28] J. Li, N. Yan, Z. Qu, S. Qiao, S. Yang, Y. Guo, P. Liu, J. Jia, *Environ. Sci. Technol.* 44 (2009) 426–431.
- [29] C. He, B. Shen, J. Chen, J. Cai, *Environ. Sci. Technol.* 48 (2014) 7891–7898.
- [30] N. Russo, D. Fino, G. Saracco, V. Specchia, *J. Catal.* 229 (2005) 459–469.
- [31] H. Xu, Z. Qu, C. Zong, W. Huang, F. Quan, N. Yan, *Environ. Sci. Technol.* (2015).
- [32] R. Zhang, N. Luo, W. Yang, N. Liu, B. Chen, *J. Mol. Catal. A: Chem.* 371 (2013) 86–93.
- [33] H. Li, C.-Y. Wu, Y. Li, J. Zhang, *Appl. Catal. B: Environ.* 111 (2012) 381–388.

- [34] R. Zhang, W. Yang, N. Luo, P. Li, Z. Lei, B. Chen, *Appl. Catal. B: Environ.* **146** (2014) 94–104.
- [35] H. Xu, J. Xie, Y. Ma, Z. Qu, S. Zhao, W. Chen, W. Huang, N. Yan, *Fuel* **140** (2015) 803–809.
- [36] H. Xu, Z. Qu, S. Zhao, J. Mei, F. Quan, N. Yan, J. Hazard. Mater. **299** (2015) 86–93.
- [37] J. Xie, H. Xu, Z. Qu, W. Huang, W. Chen, Y. Ma, S. Zhao, P. Liu, N. Yan, *J. Colloid Interface Sci.* **428** (2014) 121–127.
- [38] H. Li, C.-Y. Wu, Y. Li, L. Li, Y. Zhao, J. Zhang, J. Hazard. Mater. **243** (2012) 117–123.
- [39] S. Yang, Y. Guo, N. Yan, D. Wu, H. He, J. Xie, Z. Qu, J. Jia, *Appl. Catal. B: Environ.* **101** (2011) 698–708.
- [40] H.X. Xi, Z. Li, H.B. Zhang, X. Li, X.J. Hu, *Sep. Purif. Technol.* **31** (2003) 41–45.
- [41] Z. Li, H.J. Wang, H.X. Xi, Q.B. Xia, J.L. Han, L.A. Lu, *Adsorpt. Sci. Technol.* **21** (2003) 125–133.
- [42] R.T. Yang, R.Q. Long, J. Padin, A. Takahashi, T. Takahashi, *Ind. Eng. Chem. Res.* **38** (1999) 2726–2731.